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DESIGN OF BIO-HYBRID SURFACE ASSEMBLIES AT ENGINEERING INTERFACES

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The project is devoted to designing and fabricating flexible free-suspended nanocomposite membranes based on a bioinspired concept of snake photothermal receptors. We suggested an innovative fabrication technique which can be used to obtain robust and lightweight, *microscopic nanocomposite membranes* with extraordinary sensitivity and dynamic range. These nanomembranes with thickness of 30-50 nm and diameter of several hundred microns, which can be free-suspended over a microscopic opening were fabricated with molecular precision by time-efficient, spin-assisted layer-by-layer assembly on a sacrificial substrate. They are designed as multilayered nanocomposite films composed of polymer bilayers alternating in ordered fashion and gold nanoparticles with a diameter below 13 nm and possess unparalleled sensitivity combined with extreme robustness.

Project objectives

The main thrust of this project is the understanding the basic principles of a bio-inspired design that incorporates protein biomolecules in compliant artificial membranes situated onto engineered interfaces of silicon chips in supported and free-standing states.

Major focus areas

- Design of microelectronic-related silicon surfaces to be compatible with biological macromolecules: avoid denaturation and unfolding and control of conformation and shape of mechanosensitive channel proteins and silk proteins

- Design and synthesis of multifunctional branched molecules with selective intermolecular interactions as prospective organic templates for assembling biological and inorganic nanostructures in organized arrays

- Design and fabrication of free-suspended compliant inorganic-organic multilayered membranes serving as a sensing element of thermal microcells and testing their micromechanical properties and sensitivity

- Design and preliminary studies of tri-layered (polymer-metal-silicon) microcantilever beams for un-cooled thermal sensor arrays (in collaboration with Agiltron, supported by AFOSR-STTR Phase I, II)

Development of a new instrument based on combined NSOM-AFM-Raman microscopy for concurrent detection of surface nanostructural morphology, chemical composition, and optical properties (supported by current AFOSR-DURIP program)

Major accomplishments (for complete results see a full list of refereed papers enclosed)

- We demonstrated that the shape of MscL membrane proteins changes dramatically depending upon and the surface tension of the supporting organic layer. We suggest that this observation is consistent with conformation reorganizations associated with the iris-like expansion proposed for the gating of the MscL molecules. This is the first direct observation of the characteristic, multi-stage gating of the MscL proteins that includes close-pore, close-extended, and open-pore states caused by dramatic conformational transformation initiated by local stresses within cell membranes (*J. Am. Chem. Soc.*, **2003**, *125*, 12722).

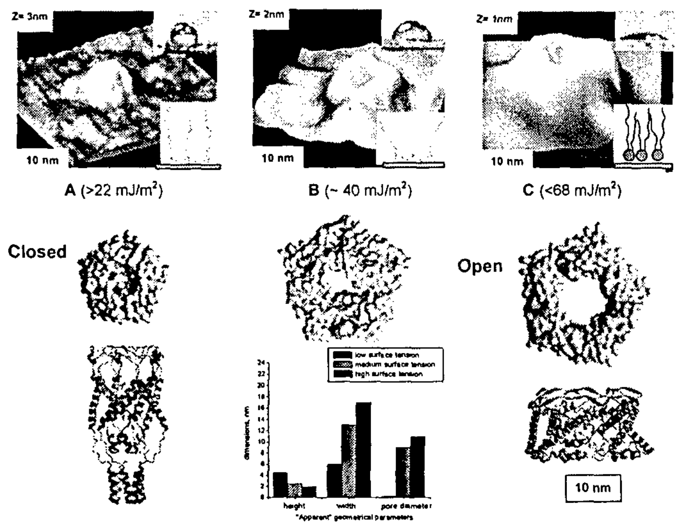


Fig. 1. Controlling MscL state with surface tension.

- We found that the amplification of weak multiple interactions between numerous peripheral branches of irregular, flexible, polydisperse, and highly branched molecules can facilitate their self-assembly into nanofibrillar micellar structures at solid surfaces and the formation of perfect long microfibers in the course of crystallization from solution (Fig. 2). The core-shell architecture of the amphiphilic dendritic molecules provides exceptional stability of one-dimensional nanofibrillar structures. The critical condition for the formation of the nanofibrillar structures is the presence of both alkyl tails in the outer shell and amine groups in the core/inner shell (Fig. 3). The multiple intermolecular hydrogen bonding and polar interactions between flexible cores

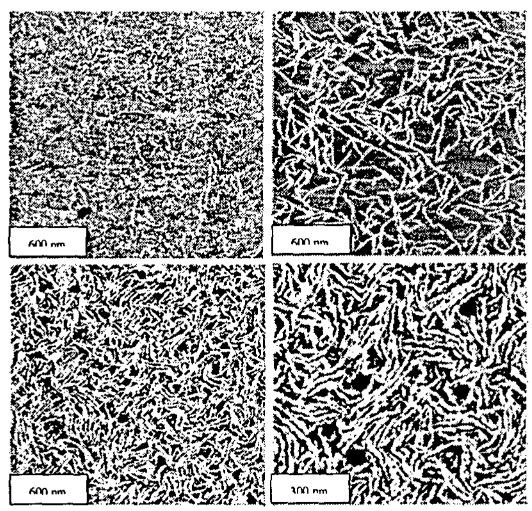


Fig. 2. AFM images of polymeric nanofibers.

stabilize these nanofibers and make them *robust albeit flexible*. This example demonstrates that one-dimensional supramolecular assembling at different spatial scales can be achieved without a tedious, multi-step synthesis of shape-persistent

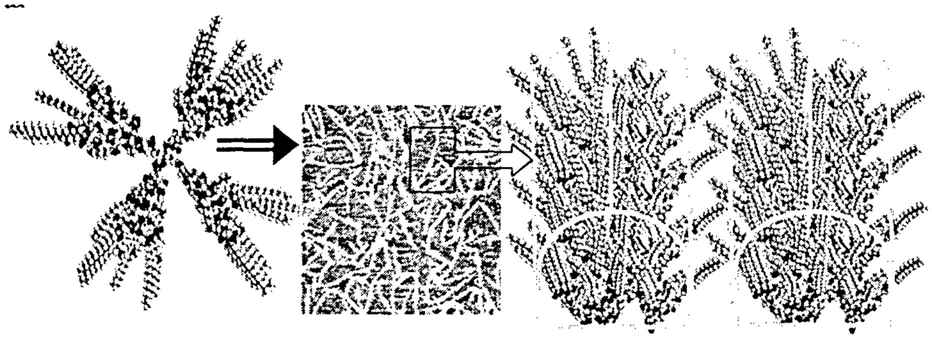


Fig. 3. Molecular model (left) of multifunctionalized branched molecules, nanofibrill formation (center, 700 nmx700 nm), and models of semi-spherical microstructure suggested.

Am. Chem. Soc., **2004**,*126* , 9675*)*.

- We reported on an innovative fabrication technique which can be used to obtain compliant, robust, and lightweight, *nanocomposite membranes* with *microscopic* lateral dimensions (100-600 μm) and extraordinary sensitivity and dynamic range to external pressure. These nanoscale membranes with thickness of 30-50 nm, which can be free-suspended over a microscopic opening were fabricated with molecular precision by time-efficient, spin-assisted layer-by-layer assembly (SA LbL) on a sacrificial substrate. They are designed as multilayered nanocomposites composed of polymer bilayers alternating in ordered fashion and gold nanoparticles with a diameter below 13 nm (Fig. 4). Moreover, we demonstrated that nanocomposite membranes, with nanoscale thickness and microscopic lateral dimensions, can possess unparalleled sensitivity combined with extreme robustness.

- Unique nanostructure of these membranes responsible for these outstanding properties combines multilayered polymer organization, built-in internal stresses, functional central nanoparticle-containing layer and makes them unique candidates for a new generation of membrane-based acoustic, pressure, and temperature sensor microarrays with superior sensitivity, dynamic range, and built-in recovery ability. We believe that these compliant and highly sensitive nanomembranes are a breakthrough for applications in membrane-based sensor technology allowing dramatic miniaturization of the thermal and acoustic sensors. A unique auto-recovering ability of these membranes discovered in this study (see below) is very promising for their long-time stability (*Adv. Mater.*, **2004**, *16*, 157).

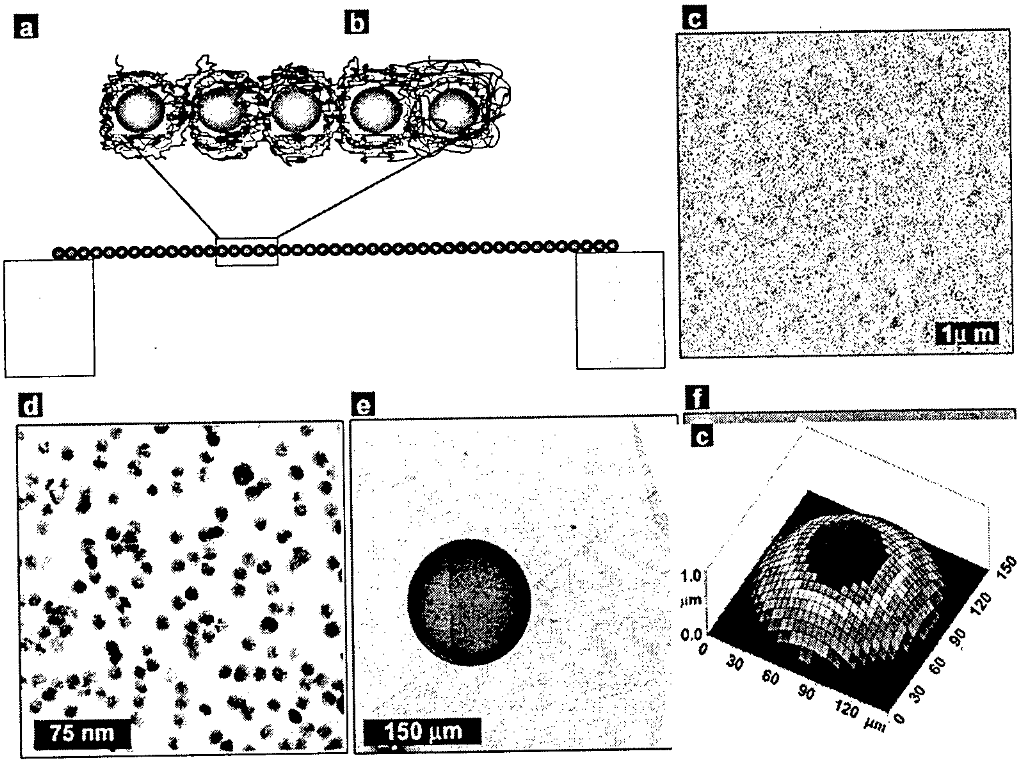
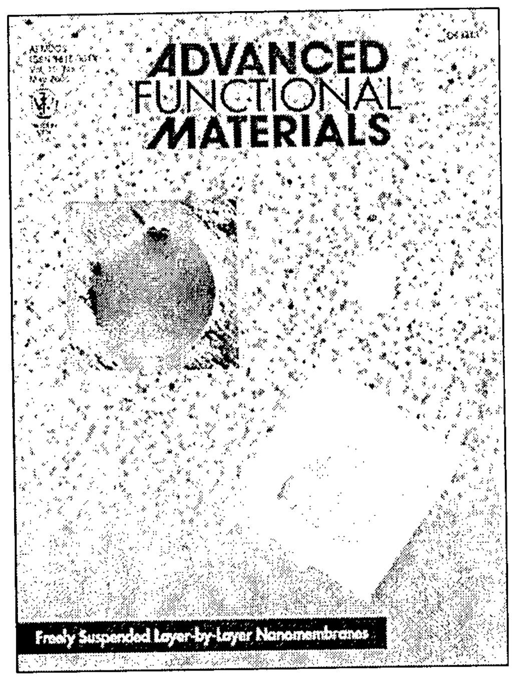


Fig. 4. Free-suspended nanomembranes (a,b), TEM images of embedded nanoparticles distribution (c,d), SEM image of membrane on copper substrate (e), and bulged nanomembranes (f).

- The internal distribution of gold nanoparticles forming chain-aggregates was suggested to be critical for outstanding robustness of these membranes and their smooth optical interference properties (*Adv. Funct. Mater.*, **2005,** *15,* 771-780, see inside cover for *Adv. Funct. Mat.*, May 2005). On the hand, comprehensive studies of extreme large and small deformations (several tens of a micron for large deflections and below 1 nanometer for small deflections) revealed a very large dynamic range (~100,000 for a membrane with a diameter of 400 μm) for stable and reversible membrane deflections under external pressure (see Fig. 5 for a combined graph with pressure-deflection variations). The



sensitivity of polymer based nanocomposite membranes evaluated as a vertical deflection per an external pressure unit exceeds significantly those known for silicon membranes especially for membranes with smaller diameters (below 100 μm) (Fig. 5) (*Nature Mater. (Cover Story)* **2004,** *3*, 721-728).

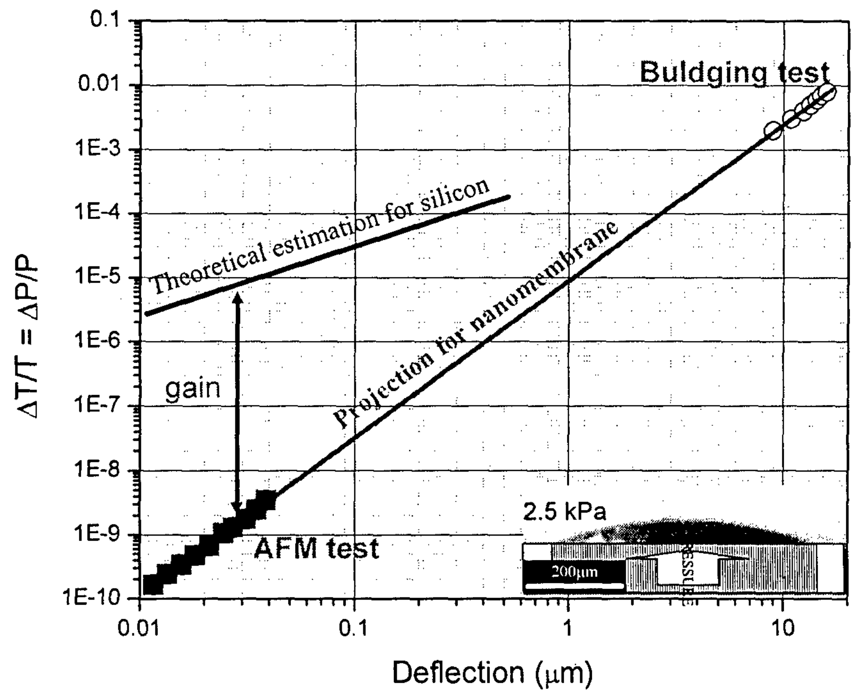
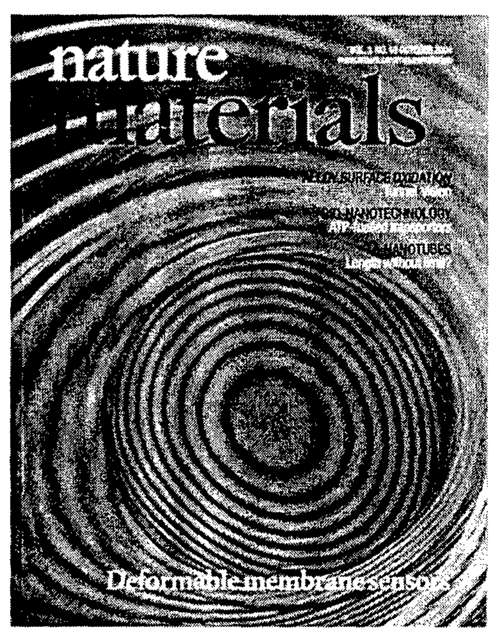


Fig. 5. Deflections of nanocomposite membranes at different pressures.

- The optical interference pattern generated within a simple interference set-up in the course of membrane deflection can be used for fast optical monitoring of their deflection state as demonstrated in a cover image for *Nature Materials (Nature Mater. (Cover Story)* **2004,** *3,* 721-728). The membrane showed a long life time exceeding a million cycle under noisy lab conditions, the ability to recover after extreme deformations (close to the ultimate strength), and excellent sealing ability of the membranes preventing gas diffusion through the membrane for the time periods of minutes-hours (*Appl. Phys. Lett.,* **2005,** *86,* 121912). Preliminary results on encapsulation of micropatterned arrays



(gold nanoparticles and carbon nanotubes) revealed that membrane gratings can be fabricated with interesting optical and mechanical properties (*Adv. Mater.* **2005,** *17*, 1669-173; *Chem. Mater.*, **2005,** *17*, 2490-2493) (further studies supported by an AFOSR renewed project (2005-2008) are in progress).

- We developed combined confocal-AFM-Raman instrument to generate high-resolution surface micromapping. As an example, patterned carbon nanotube assemblies with bent nanotube bundles were investigated with combined atomic force microscopy and confocal Raman imaging spectroscopy to identify conditions of carbon nanotubes in the bent state (Fig. 6). We showed that the tangential G-mode on Raman spectra systematically shifts downward upon nanotube bending as was predicted earlier. This lower frequency shift is attributed to the tensile stress, which results in the loosening of C–C bonds in the outer nanotube walls. Monitoring of the mechanical bending stresses of carbon nanotubes with Raman spectroscopy can be exploited for optical-mechanical sensing (*Appl. Phys. Lett.*, **2004,** *85,* 2598-2600).

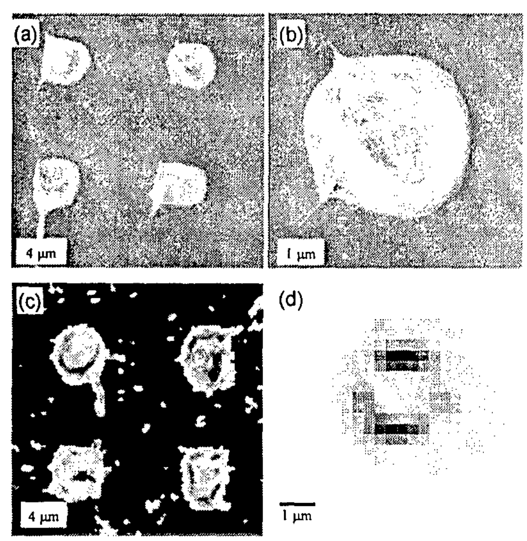


Fig. 6. (a) and (b): AFM topographical images of nest-shaped patterned nanotube assembly; (c): corresponding distribution of Raman G-line position, intensity varies from 1588 cm^{-1} (dark) to 1594 cm^{-1} (bright); (d): high resolution Raman image of the individual "nest" at 1594 cm^{-1},

4 μm

Related developments

Personnel supported/participated

Ms. M. Ornatska, Mr. M. Lemieux, Mr. M. McConney, and Ms. B. Rybak, MSE-ISU graduate students and Dr. C. Jiang and Dr. Yu. Pikus, post-doctoral researchers have been involved and supported by this project as well as other related AFOSR projects (AFOSR-STTR with Agiltron and AFOSR-DURIP). Ms. K. Bergman, an undergraduate student, conducted AFM studies of nanofibtrills.

M. Ornatska (2004) and B. Rybak (2005) have defended their MS theses. M. Ornatska continues her PhD studies and B. Rybak has been graduated in Spring 2005 and is employed by Lockheed-Martin.

17 peer-reviewed publications generated with AFOSR support have been published in top-ranked archival journals such as *Nature, Physical Review Letters, Applied Physics Letters, Advanced Materials, J. Am. Chem. Soc.*, etc.) One patent application is pending: The names of USAF collaborators from AFRL and AFIT are underlined.

1. C. Jiang, B. M. Rybak, S. Markutsya, P. E. Kladitis, V. V. Tsukruk, Self-recovery of Nanocomposite Nanomembranes, *Appl. Phys. Lett.*, **2005**, *86*, 121912.
2. C. Jiang, S. Markutsya, H. Shulha, V. V. Tsukruk, Freely Suspended Gold Nanoparticles Arrays, *Adv. Mater.***2005**, *17*, 1669-173.
3. S. Markutsya, C. Jiang, Y. Pikus, V. V. Tsukruk, Free-standing multilayered nanocomposites films as highly sensitive nanomembranes, *Adv. Funct. Mater.*, **2005**, *15*, 771-780.
4. C. Jiang, S. Markutsya, Y. Pikus, V. V. Tsukruk, Freely Suspended Nanocomposite Membranes as Highly-Sensitive Sensors, *Nature Mater. (Cover Story)* **2004**, *3*, 721-728.
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7. H. Ko, S. Peleshanko, V. V. Tsukruk, Combing And Bending Of Carbon Nanotube Arrays With Confined Microfluidic Flow On Patterned Surfaces, *J. Phys. Chem.*, **2004**, *108*, 4385-4393.
8. M. Ornatska, S. Peleshanko, K. L. Genson, B. Rybak, K. N. Bergman, V. V. Tsukruk, Assembling amphiphilic highly branched molecules in supramolecular nanofibers, *J. Am. Chem. Soc.*, **2004**, *126*, 9675.
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10. M. Ornatska, S. Peleshanko, B. Rybak, J. Holzmueller, V. V. Tsukruk, Supramolecular multi-scale fibers through one-dimensional assembly of dendritic molecules, *Adv. Mater.* **2004,** *16,* 2206-2211.
11. C. Jiang, S. Markutsya, V. V. Tsukruk, Compliant, Robust, and Truly Nanoscale Free-Standing Multilayer Films Fabricated using Spin-Assisted Layer-by-Layer Assembly, *Adv. Mater.,* **2004,** *16*, 157.
12. C. Jiang, S. Markutsya, V. V. Tsukruk Collective and Individual Plasmon Resonances in Nanoparticle Films Obtained by Spin-Assisted Layer-by-Layer Assembly, *Langmuir,* **2004,** *20*, 882.
13. Luzinov, I. S. Minko, V. V. Tsukruk, Adaptive and Responsive Surfaces Through Controlled Reorganization Of Interfacial Polymer Layers, *Prog. Polym. Sci.* **2004,** *29,* 635.
14. M. Ornatska, S. E. Jones, R. R. Naik, M. Stone, V. V. Tsukruk, Biomolecular Stress-Sensitive Gauges: Surface-Mediated Immobilization of Mechanosensitive Membrane Protein, *J. Am. Chem. Soc.* **2003,** *125*, 12722.
15. Tsukruk, M. Ornatska, A. Sidorenko, Synthetic and bio-hybrid nanoscale layers with tailored surface functionalities, *Progr. Organic Coatings,* **2003,** *47,* 288.
16. D. Julthongpiput, Y-H. Lin, J. Teng, E. R. Zubarev, V. V. Tsukruk Y-shaped Amphiphilic Brushes with Switchable Micellar Surface Structures, *J. Am. Chem. Soc.* **2003,** *125*, 15912.
17. V. Gorbunov, N. Fuchigami, M. Stone, M. Grace V. V. Tsukruk, Biological thermal detection: Micromechanical and microthermal properties of biological infrared receptors, *Biomacromolecules,* **2002**, *3*, 106.

A patent application "Flexible Nanocomposite Membranes" is pending (filled on September 24 2004 by ISU)

25 oral and poster presentations including 14 invited talks have been delivered at ACS, MRS, APS, and other national and international meetings and seminars by the PI and his students.

International and national-wide publicity of the results generated with AFOSR support is facilitated by *two cover stories and six articles* in professional magazines of relevant papers published in 2002-2005. These publicity ("we are in news") show a wide spread excitement in a scientific community with the results presented by the PI's group:

Cover story in *Nature Materials*, October 2004

Inside Cover in *Advanced Functional Materials*, May 2005

T. Xu, CNT arrays encapsulated into freely suspended flexible films, *MRS Bull.*, **2005,** *30(7)*, 501. http://www.mrs.org/publications/bulletin/2005/jul/july05_researchers.pdf

Freemantle, M. Nanocomposite membranes are highly sensitive, *Chem. Eng. News,* **2004,** *82(42),* p. 46; http://pubs.acs.org/cen/ncw2004/8242scic.html

N. Kotov, Nanocomposites are stretched thin, *Nature Materials,* **2004,** *3,* 669-671 http://www.nature.com/cgi-taf/DynaPage.taf?file=/nmat/journal/v3/n10/full/nmat1224.html

C. Sealy, Bending over backwards for nanotubes. *Materials Today,* **2004**, 5, p. 9.

Freemantle, M. Snake-inspired nanoscale films, *Chem. Eng. News,* **2004,** *82(16),* 44; http://pubs.acs.org/cen/nlw/8216sci3.html#Anchor-37516

R. C. Willis, A "Sense" of Snakes: IR Detection, *Today's Chemist at Work,* **2002**, *11(3),* 12: http://pubs.acs.org/subscribe/journals/tcaw/11/i03/html/03update.html

Significant external interactions/collaboration activities related to the project

1. Collaboration with M. Stone and R. Naik (AFRL) on snake membranes and MscL proteins resulted in two joint publications.
2. Collaboration with P. Kladitis (AFIT) on interference microscopy of suspended membranes resulted in one joint publication.
3. PI's students visited WPAFB and Agiltron (3 times) for joint research and results discussion.
4. AFOSR-STTR project started with Agiltron on un-cooled thermal sensor arrays, PI visited Agiltron several times and discussed research directions/results.
5. DARPA project with Agiltron on membrane arrays was initiated.
6. AFOSR-DURIP project was completed and a unique instrumentation for combined confocal Raman-AFM studies has been assembled and used for membrane studies.

REPORT DOCUMENTATION PAGE

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1. REPORT DATE *(13/07/2005)*	2. REPORT TYPE	3. DATES COVERED *(06/2002-05/2005)*

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5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

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5e. TASK NUMBER

5f. WORK UNIT NUMBER

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13. SUPPLEMENTARY NOTES

NA

14. ABSTRACT

The project is devoted to designing and fabricating flexible free-suspended nanocomposite membranes based on a bioinspired concept of snake photothermal receptors. We suggested an innovative fabrication technique which can be used to obtain robust and lightweight, *microscopic nanocomposite membranes* with extraordinary sensitivity and dynamic range. These nanomembranes with thickness of 30-50 nm, which can be free-suspended over a microscopic opening were fabricated with molecular precision by time-efficient, spin-assisted layer-by-layer assembly on a sacrificial substrate. They are designed as multilayered nanocomposites composed of polymer bilayers alternating in ordered fashion and gold nanoparticles with a diameter below 13 nm and possess unparalleled sensitivity combined with extreme robustness.

15. SUBJECT TERMS

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